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THEORETICAL AND EXPERIMENTAL INVESTIGATION OF REACTION MECHANIS--ETC(U)
OCT 77 H EYRING, R KELLEY

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Research efforts on the formation and analysis of polymer carbon electrodes to serve as oxygen electrodes and on the synthesis of porphyrins and porphyrazines for study as oxygen reduction catalysts in conjunction with polymer carbon electrodes are described. The report also presents a very simple but highly accurate model of detonation which ignores viscosity, diffusion, and heat conduction. The salient features of the model are unimolecular reaction, kinetics with starvation, balance laws, and a covolume equation of state.			

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FINAL REPORT

Henry Eyring, Principal Investigator

October 19, 1977

U. S. Army Research Office

The progress reports we have sent in during the tenure of this grant will provide material not repeated here. Two phases of the grant not previously discussed and still in progress will be presented first in some detail.

MECHANISTIC STUDY OF POLYMER CARBON ELECTRODES

FOR USE IN THE HYDROGEN OXYGEN FUEL CELL.

(The work of Robert Kelley toward his Doctoral Degree and supported by this grant)

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FINAL REPORT

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"Slow vibrationally activated reactions at high temperatures", Henry Eyring, Priestley Medal Address, (C&EN, April 14, 1975) 27-31.

"A Limitation to the Mixed Potential Concept of Metal Corrosion", T. N. Andersen, M. H. Ghandehari, and H. Eyring, J. Electrochemical Society 122, 1580-1585 (1975).

"The Electrochemical Reduction of Oxygen on Copper in Dilute Sulphuric Acid Solutions", M. H. Ghandehari, T. N. Andersen and H. Eyring, Corr. Sci. 16, 123-135 (1976).

"A Limitation to the Mixed Potential Concept of Metal Corrosion", T. N. Andersen, M. H. Ghandehari, and H. Eyring, J. Electrochem. Soc. 123, 843-845 (1976).

"Significant structure theory applied to phase separation", by Suck-Hyun Lee, Mu Shik Jhon and Henry Eyring, Proc. Natl. Acad. Sci. USA 74, 10-12 (1977).

"Effects of Oxygen on the Mechanism of Cadmium Dissolution in Sulfate Solutions", by T. N. Andersen, M. H. Ghandehari, E. Feng, and H. Eyring, J. Electrochem. Soc. 124, 977-981 (1977).

"Starvation Kinetics". Bond-Breaking denied adequate activation by collision can be starved in many ways." (Submitted to SCIENCE, 1977).

FINAL REPORT (cont.)

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Formation and Analysis of Polymer Carbon Electrodes to Serve as Oxygen Electrodes

A Lindberg Control Console/Programmer System which provides for a ramped temperature rise at a known rate, and the necessary tube furnace has been purchased and set up. This provides for a temperature span of from room temperature to 1500°C. Furfuryl alcohol polymers have been formed into rods of 1.5 cm diameter, sliced into 1-2 mm thick discs, followed by pyrolysis at a known rate to various maximum temperatures. The electrodes are then polished and mounted for further electrochemical study. The treatment temperatures cover the range 300°C to 1500°C, with special emphasis on the range of 400°C to 600°C in which the electrical properties of the polymer carbons experience the greatest change.

A special three compartment electrolytic cell and a thermostated bath to control the temperature have been built to study the mechanism of O₂ reduction on these polymer carbons.

An apparatus has also been set up to measure the conductivities of these polymer carbons at various temperatures.

Under construction is a vacuum-line set-up to measure gas absorption on these polymer carbons in order to calculate the Brunauer-Emmett and Teller surface area and the pore size. This information will be used to study the molecular sieve properties of these polymer carbons.

Oxygen Reduction Catalysts

All necessary chemicals and procedures have been acquired for the synthesis of the following porphyrins and porphyrazines for study as O₂-reduction catalysts in conjunction with the polymer carbon electrodes; Porphyrazine's (Mn, Ni, Fe, Co)-; Tetra-2,3-(Dibenzobarreleno); Octakis (p-t-Butyl Phenyl); Tetrakis (t,t'-Di-t-Butyl-2,2'=Biphenylene); Tetra-4-t-Butyl Phthalocyanine; Tetra-6-t-Butyl-2,3-Naphthalocyanine; Porphyrins (Mn, Ni, Fe, Co) - Tetra Phenyl; P-Carboxy Tetraphenyl;

Tetrakis p-N(CH₃)₂ Tetraphenyl; Tetrakis p-OH-Tetraphenyl; Tetrakis p-OCH₃ Tetraphenyl; Tetrakis p-CH₃ Tetraphenyl; Tetrakis p-NO₂ Tetraphenyl; Tetrakis p-C₂H₅ Tetraphenyl; Tetrakis p-n-Propyl Tetraphenyl; Tetrakis p-Isopropyl Tetraphenyl; Tetrakis p-t-Butyl Tetraphenyl; Tetrakis p-Diphenyl Tetraphenyl; Tetrakis p-Terphenyl Tetraphenyl.

The structures of these catalysts are shown in the following pages. The compounds are grouped according to the common principle characteristics to be investigated. As examples, the Co complexes are given.

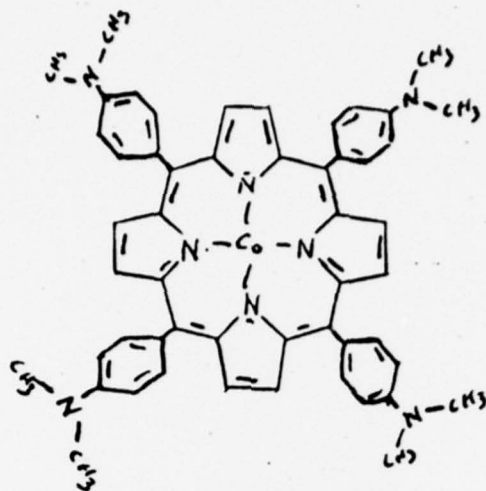
The complexes Co(Tetrakis p-N(CH₃)₂) Tetra-Phenyl Porphyrin thru Co (Tetrakis Penta Fluoro) Tetra-Phenyl Porphyrin are arranged in order of decreasing electron donor ability.

The complexes Co(p-Ethyl) TetraPhenyl Porphyrin thru Co-(p-t-Butyl) Tetra-Biphenyl Porphyrin are grouped according to increased branching and size of the substituents attached to the para position of the Phenyl groups. Electro-chemical stability is the principle characteristic to be investigated in this series.

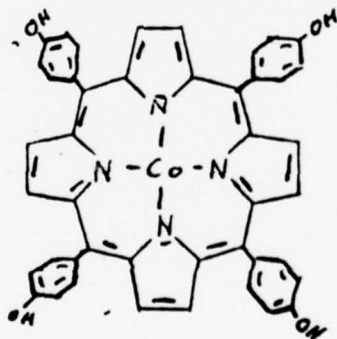
The complexes Co-Tetra-Terphenyl Porphyrin thru Co-Tetra-2,3-(Dibenzo-Barreleno) Porphyrazine exhibit a greater amount of π bonding and resonance stability in their structure. How such factors contribute to their catalytic properties toward O₂ reduction and their stability as adsorbed complexes on the carbon surface are the principle points to be investigated here.

The compounds listed below are not available commercially but methods of synthesis of all of them have been found and assembled. As many will be tested as time, funding and favorable indications suggest. Out of it will come a better understanding of the oxygen electrode and improved electrodes.

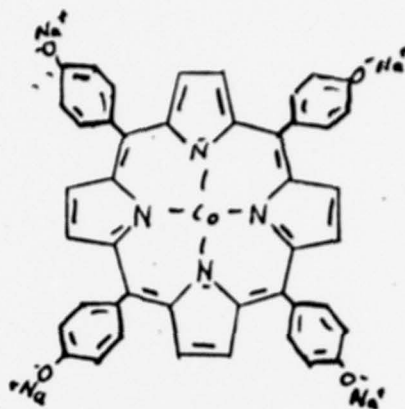
Co (Tetrakis p-N(CH₃)₂) Tetra-Phenyl Porphyrin



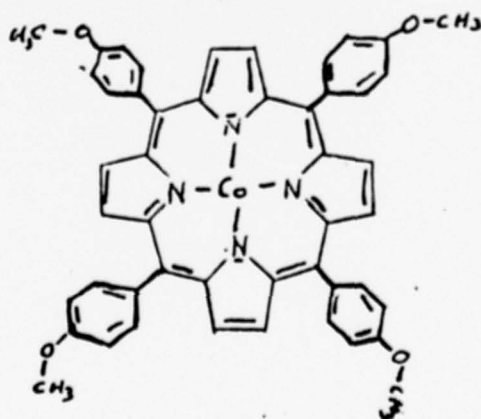
Co(Tetrakis p-OH) Tetra-Phenyl Porphyrin



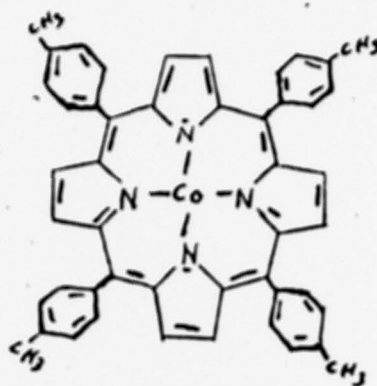
Co (Tetrakis p-O⁻Na⁺) Tetra-Phenyl Porphyrin



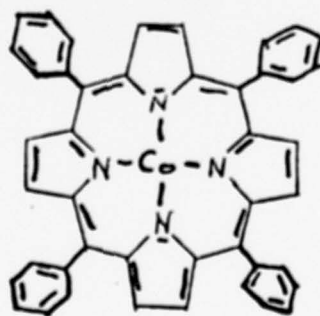
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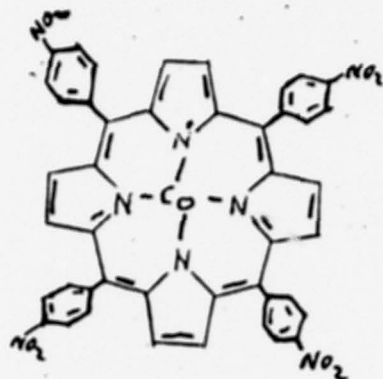
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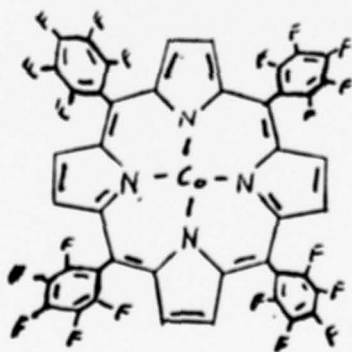
Co-Tetra-Phenyl Porphyrin



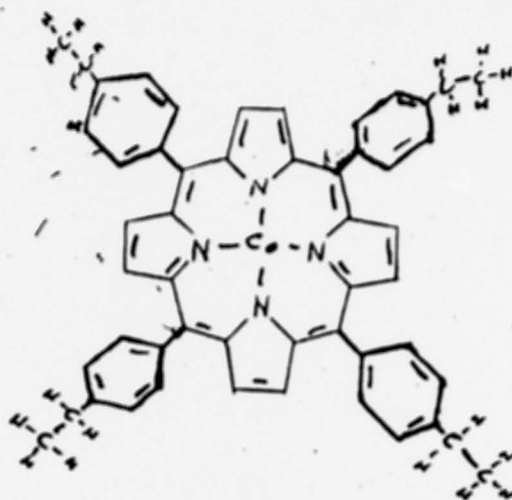
Co (Tetrakis p-NO₂) Tetra-Phenyl Porphyrin



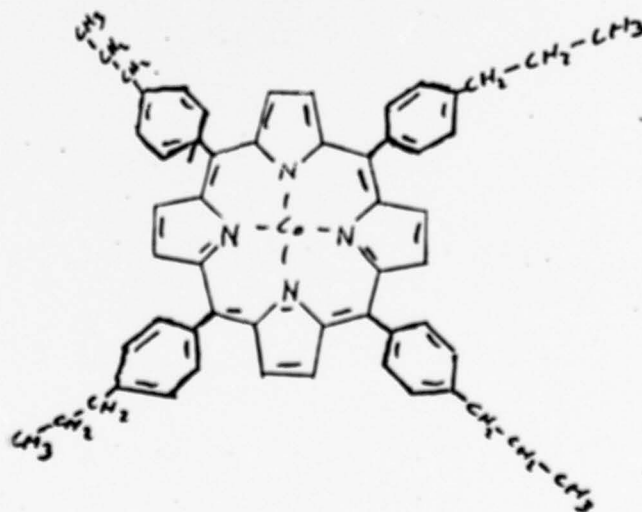
Co (Tetrakis Penta Fluoro) Tetra-Phenyl Porphyrin



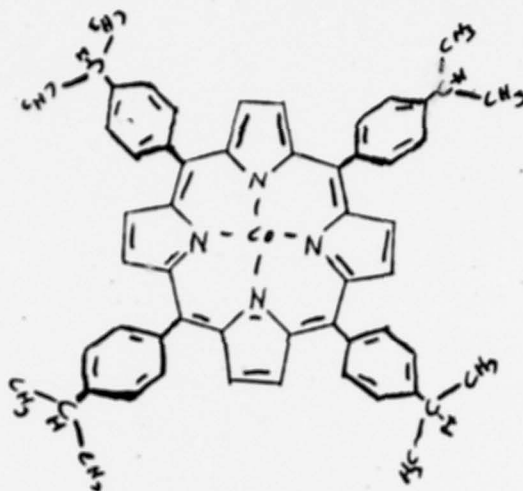
Co-(p-Ethyl) Tetra-Phenyl Porphyrin



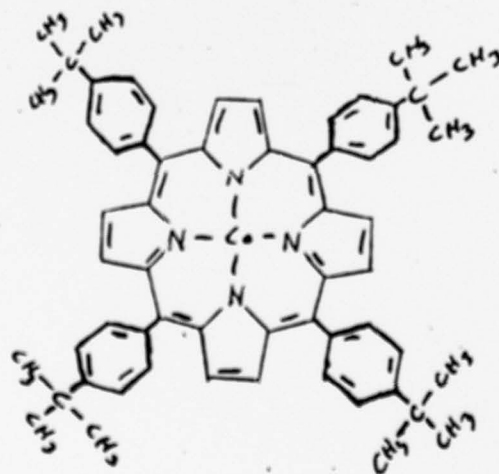
Co-(p-n-Propyl) Tetra-Phenyl Porphyrin



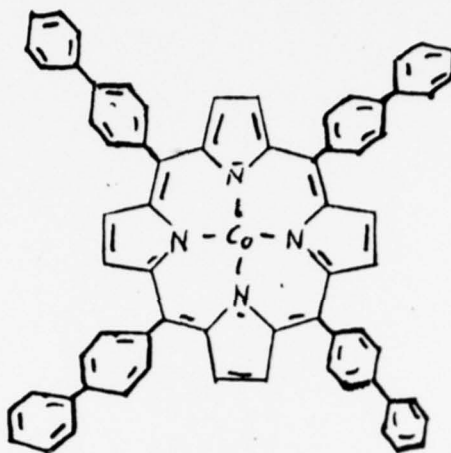
Co-(p-Isopropyl) Tetra-Phenyl Porphyrin



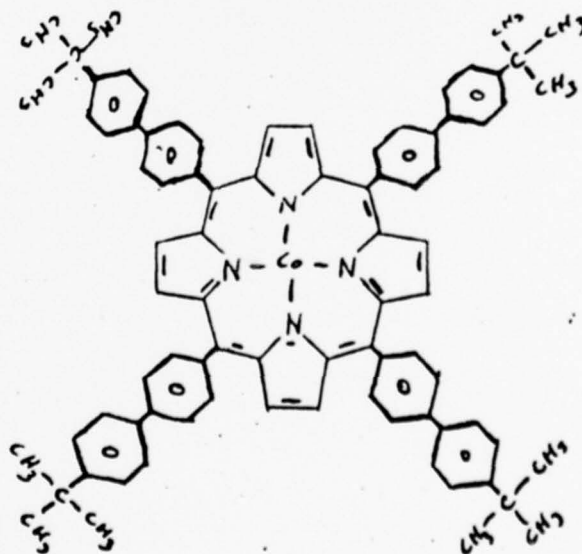
Co-(p-t-Butyl) Tetra-Phenyl Porphyrin



Co-Tetra (p-Biphenyl) Porphyrin

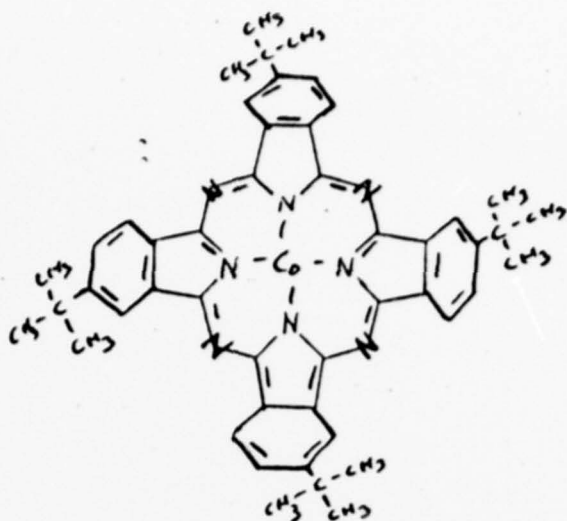


Co-(p-t-Butyl) Tetra-Biphenyl Porphyrin

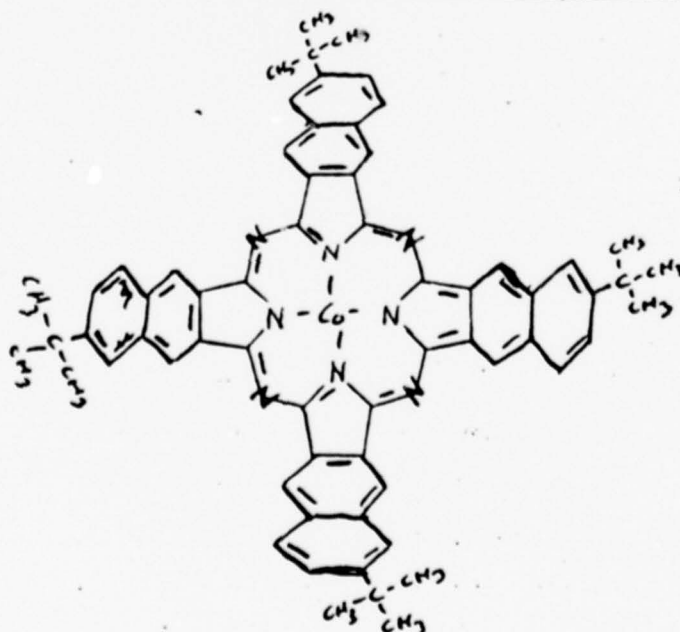


The diagram shows a central cobalt (Co) atom coordinated by four nitrogen (N) atoms in a square planar arrangement. The Co-N bonds are represented by dashed lines. The four nitrogen atoms are part of a macrocyclic ligand that forms a porphyrin-like core. Each of the four meso-positions of the macrocycle is substituted with a long, branched side chain. Each side chain consists of three octagons connected in a linear fashion, with a single bond connecting the side chain to the macrocycle. The octagons are drawn with internal double bonds, suggesting they are cyclooctatetraenes. The overall structure is highly symmetrical.

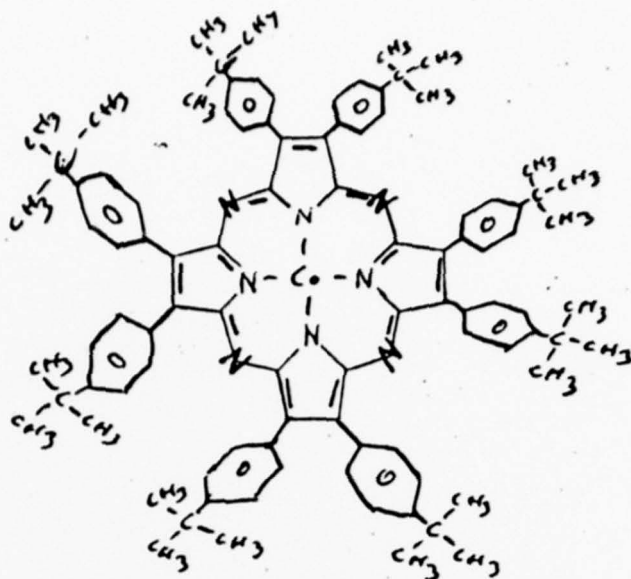
Co-Tetra-4-t-Butyl Phthalocyanine



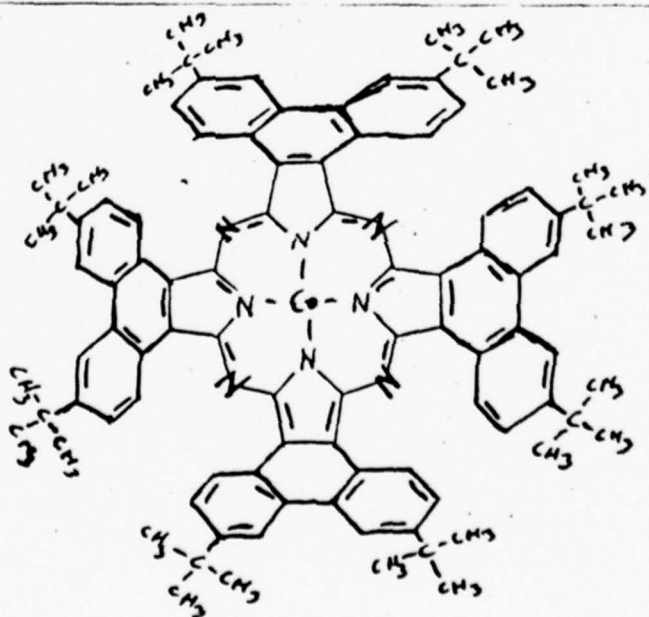
Co-Tetra-6-t-Butyl-2,3-Naphthalocyanine



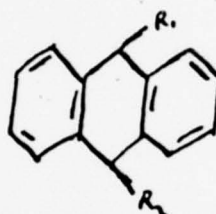
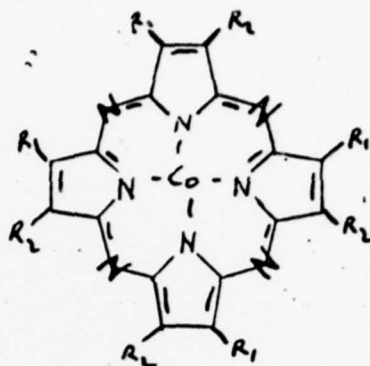
Co-Octakis(p-t-Butyl Phenyl) Porphyrazine



Co-Tetrakis(5,5'-di-t-Butyl-2)2'-Biphenylene Porphyrazine



Co-Tetra-2,3-(Dibenzobarreleno) Porphyrazine



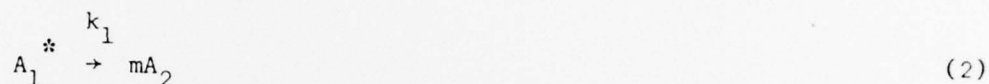
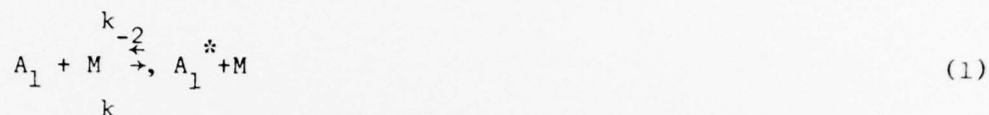
A Model of 1-D Detonation Based on the Kinetics of a
Unimolecular Reaction and on the Concept of Energy Starvation
(Program begun by Paul J. Blatz and Henry Eyring and continuing.)

I. Introduction

The concept of detonation implies the propagation of a shock wave from a high pressure region of low chemical energy into a low pressure region of high chemical energy. Two other concepts dictate or determine the speed of this wave, - one is the set of balance laws of mass, energy, and momentum, - the other is the kinetics of decomposition of the energy rich material. The idea of "starvation kinetics" introduced by one of us⁽¹²⁾ simply means that waves cannot travel faster than that speed which is determined by the rate at which the wave front picks up energy from the energy-rich material, whereas the energy-rich material cannot release energy faster than the rate at which it picks up heat and work from the advancing high-pressure front. In a non-detonable material, the wave speed is fixed by the laws of thermohydrodynamics. In a detonable material, the wave is capable of going much faster according to the balance laws, but does not, indeed, reach its optimum thermohydrodynamic speed, because of the limitations imposed upon it by the kinetics of decomposition. This limitation is, basically speaking, a statistical one. The energy fed into the "cold" but energy-rich molecule distributes itself amongst a large number of degrees of freedom. Furthermore, the energy of any one degree of freedom must exceed a critical value before decomposition takes place. This "rattling around" of energy in non-decomposing degrees of freedom leads to what we call starvation kinetics. In this report, we present a very simple but highly accurate model of detonation. We ignore viscosity, diffusion, and heat conduction. The salient features, as already indicated, are unimolecular reaction, kinetics with starvation, the balance laws, and a covolume equation of state. In the next section, we present the pertinent mathematics.

II. The 1-D Model

We imagine a two-component system. Component designated by subscript 1 is the high-energy molecule A_1 . Component designated by subscript 2 is the low-energy diatomic molecule A_2 . Component 1 goes to compound 2 by the reaction scheme.⁽³⁾



where m is the number of diatomic molecules into which A_1 decomposes.

The overall rate of the reaction scheme is given by:

$$r = \frac{k_1 k_2 n_1}{k_{-2} + k_1/n} \quad (3)$$

where n_i is the number of moles/unit volume of specie "i".

$$n = \sum_{i=1}^2 n_i \quad (4)$$

$$k_1 = \frac{kT}{h} e^{-(s+E/RT)} \sum_{i=0}^{s-1} \frac{(E/RT)^i}{i!} \quad (5)$$

$$k_1 = \frac{kT}{h} e^{-\Delta G^\ddagger/RT} \quad (6)$$

$$k_2 = \frac{kT}{h} e^{+\Delta G^\ddagger/RT} \quad (7)$$

and where s is the number of vibrational degrees of freedom in communication with the bond to be broken.

The component A_1 has $2m$ atoms or $6m$ degrees of freedom. Therefore

$$6m = 3 + 3 + s$$

or

$$s = 6(m-1) \quad (8)$$

The component A_2 has 6 degrees of freedom. Thus the specific heats, because of the high temperature, are closely given by:

$$C_{v1} = (6m - 3)R$$

$$C_{v2} = 7/2 R \quad (10)$$

and the molar internal energies are approximated by:

$$U_1 = U_{10} + (6m - 3) R(T - T_o) \quad (11)$$

$$U_2 = U_{20} + 7/2 R(T - T_o) \quad (12)$$

Furthermore

$$U_{10} - m U_{20} = E \quad (13)$$

the energy of dissociation!

The molecular weights of A_1 and A_2 are designated by M_1 , M_2 and we note that:

$$M_1 = m M_2 \quad (14)$$

The equations-of-state for each component are taken in the form (cf. Appendix) namely:

$$\left. \begin{aligned} p_i &= n_i RT \left(1 + \frac{b_i n}{1 - \sum_j b_j n_j} \right) \\ p &= \frac{nRT}{1 - \sum_j b_j n_j} \end{aligned} \right\} \quad (15)$$

where b_i is the "hard" volume/mole. $\frac{RT}{p}$ is the "soft" volume/mole. p_i is the partial pressure.

The balance laws take the form⁽⁴⁾:

$$\frac{\partial}{\partial t} (M_1 n_1) + \frac{\partial}{\partial x} (M_1 n_1 v_1) = -\Gamma M_1 \quad (16)$$

$$\frac{\partial}{\partial t} (M_2 n_2) + \frac{\partial}{\partial x} (M_2 n_2 v_2) = m \Gamma M_2 \quad (17)$$

$$\frac{\partial}{\partial t} (M_1 v_1 n_1) + \frac{\partial}{\partial x} (M_1 v_1 n_1 v_1 + P_1) = -\Gamma M_1 v_1 \quad (18)$$

$$\frac{\partial}{\partial t} (M_2 v_2 n_2) + \frac{\partial}{\partial x} (M_2 v_2 n_2 v_2 + P_2) = m \Gamma M_2 v_2 \quad (19)$$

$$\frac{\partial}{\partial t} (U_1 n_1 + U_2 n_2) + \frac{\partial}{\partial x} (U_1 n_1 v_1 + U_2 n_2 v_2 + P_1 v_1 + P_2 v_2) = -\Gamma U_1 + m \Gamma U_2 \quad (20)$$

The five equations (16-20) possess real characteristics and therefore always admit a steady wave characterized by a speed D . We can determine the speed

analytically along with the shape of the wave by replacing the time derivative

$$\frac{\partial}{\partial t} \text{ by } -D \frac{\partial}{\partial x}$$

after which we arrive at five coupled nonlinear first order ordinary differential equations in the unknowns $\{n_1, n_2, v_1, v_2, \text{ and } T\}$.

The system depends on the following set of adjustable parameters:

$$\{M_2, m, E, b_1, b_2, \Delta G^\ddagger, T_0\}$$

If we denote the low-pressure energy-rich limit at $(x \rightarrow \infty)$ by the subscript zero, then the boundary conditions are:

$$n_{10} = \frac{p_{10}}{M_1}, \text{ which is given.}$$

$$n_{20} = 0$$

$$T_0 = \text{the unshocked temperature.}$$

$$v_{10} = 0$$

Likewise if we denote the high-pressure low-energy limit at $(x \rightarrow -\infty)$ by the subscript one, then the boundary conditions are:

$$n_{11} = 0$$

$$n_{21} = \frac{p_{21}}{M_2}, \text{ which is given}$$

Only one of these two conditions along with the other four form the complete set of determinators for the two-point boundary-value problem. The other condition above falls out.

The adjustable parameters which most concern us are $\{b_1, E, m, \text{ and } \Delta G^\ddagger\}$. The other three parameters are pretty well boxed in by nature, namely:

$$T_o = 300^\circ\text{K}$$

$$M_2 \approx 30 \text{ g/g mole}$$

$$b_2 \approx .01 \text{ l/g mole}$$

III. Conclusions

We are soliciting support to study the sensitivity of the scheme(16-20) to the four parameters b_1 , E , ΔG^\ddagger , and m or s . The results of the integration can be simplified since x is an ignorable coordinate, which means that we can plot $\{n_1, n_2, v_1$ and $v_2\}$ or their equivalent on a temperature or pressure scale. Over and above what we plan to learn from the inclusion of the energy-rattle-around factor displayed in equation (5), we also are interested in displaying the shape of the temperature profile and the profile of total moles of gas/unit volume. Neither of these quantities has hitherto been successfully predicted.

In addition we will present both an analytical expression for the characteristic speed D as well as a numerical study of its sensitivities to the seven parameters of the system.

Along with the velocity, density, and temperature profiles, we are interested in the "snuff-out" point, namely that set of conditions under which the detonation wave cannot be propagated. This will fall out both from the study of the characteristics of the differential equations as well as from the computational study of the sensitivity to the seven parameters.

We plan a follow-on program in which an analysis of nonsteady, purely radial wave propagation is carried out and used to determine the characteristic radial speed. We will then carry out a perturbation analysis to determine radial loss in the propagation of a "plane" wave in a cylinder of finite diameter.

This result will be checked against the Eyring, Powell, Duffey, Parlin model which arrives at the answer:

$$\frac{D^*}{D} = 1 + \frac{a}{d} \quad (21)$$

where

a = Chapman-Jouget zone length

d = charge diameter

D^* = hydrodynamic detonation velocity

D = detonation velocity in a charge of finite diameter

In arriving at the 1-D model described above, we have invoked a number of simplifying assumptions in order to simplify the overall mathematical structure of the scheme which will be computerized. These assumptions were made with the realization that the removal of them can be done in a later follow-on program, and that the priority to be assigned to their individual removals will in turn be guided by the results of the first computer studies. In other words, we are setting the stage for gradually incorporating more and more complexity into the model. Let us now review these assumptions and indicate how they might be removed.

1. Constancy of specific heat

We have available an Einstein theory, a Debye theory, and a Blackman theory of specific heat in order of increasing complexity. In the simplest of these, namely the Einstein theory, the specific heat is given by

$$C_{vi} = \prod_{j=1}^{s_i} \left(\frac{\frac{h \nu_{is}}{2kT}}{\frac{h \nu_{ij}}{sh \frac{h \nu_{ij}}{2kT}}} \right)^3 \quad (22)$$

We have used the high temperature limit of (22). There is no problem in programming the full equation. We must then provide an additional set of parameters $\{\nu_{ij}\}$.

2. The Covolume equation-of state

The explosive molecules are actually in the condensed state in the ambient region, the decomposition products are highly pressurized gas. Together the mixture is probably best described as a liquid with gas-like degrees of freedom allowed. Such a mixture is best described by the significant structures theory,⁽⁵⁾ and this can readily be incorporated into the computer code. Again more parameters are added to the sensitivity study.

3. Neglect of heat transfer, diffusion, and viscosity

Of these three effects, we feel that the most important one to treat first is heat transfer. This effect adds to the righthand side of the energy balance a term of the form

$$- \nabla \cdot \vec{q}$$

where

$$\vec{q} = - \lambda \nabla T$$

and where λ is the thermal conductivity. The incorporation of this term has an important effect upon the properties of the differential equations. It changes them from completely hyperbolic to parabolic-hyperbolic. The heat flow vector \vec{q} introduces further dissipation and broadens further the shock wave. Just how much broadening is important to determine.

4. The Lumped-molecule kinetic scheme

The unimolecular reaction kinetics used in this treatment is one in which the various molecular species of decomposition have been lumped into one average diatomic molecule. In other words, we assume that there exists a homodiatom molecule whose molecular weight corresponds to the average

molecular weight of a combustion gas mixture comprised of $\{CO, H_2O, CO_2, H_2, O_2, O, OH, N_2, \dots\}$. We feel that, if the approximate program based on $(A_1 \rightarrow mA_2)$ turn out to be successful, then it can readily be generalized to a more elaborate reaction scheme and coupled with existing order available today for the determination of multicomponent combustion gas equilibria such as that of Johnson, Danzig, and White⁽⁶⁾, and Blatz and Wrobel⁽⁷⁾.

Appendix

The covolume equation-of-state (otherwise known as Abels' equation) is simply:

$$p(V - B) = N R T \quad (1a)$$

where B is the volume at which $P \rightarrow \infty$. We call this the "hard" volume. Let us denote

$$n = \frac{N}{V} \quad (2a)$$

the number of moles/volume and

$$b = \frac{B}{N} \quad (3a)$$

the "hard" volume/mole. Then (1a) can be rewritten in the form for a one-component gas:

$$P(1 - b n) = n R T \quad (4a)$$

In the case of a multicomponent mixture, the total pressure is given by

$$P(1 - \sum b_i n_i) = n R T \quad (5a)$$

where

$$n = \sum n_i \quad (6a)$$

In writing (5a) we have assumed that the various "hard" volumes $\{b_i\}$ add linearly. We now rewrite (5a) in the form:

$$p = \sum n_i (RT + b_i P) \quad (7a)$$

Then the partial pressure is obtained by dropping the summation sign, which again invokes the assumption of linear additivity in exactly the same fashion as Dalton did for a mixture of perfect gases. Thus we have

$$p_i = n_i (RT + b_i P). \quad (8a)$$

After eliminating p between (7a) and (8a), we recover (15) of the main text.

References

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Abstracts from previous publications

"Fall-Off from Extrapolated Values of All Chemical Reactions at Very High Temperatures", by Henry Eyring and An-Lu Leu, Proc. Natl. Acad. Sci. USA 72, 1717-1719 (May 1975).

At high temperatures the breaking of chemical bonds becomes relatively easy and the slow step in a chemical reaction shifts to the rate at which energy can seep into the bond that is to break. This has been observed by various investigators. A new general theory of reactions is developed here to explain this limiting rate at high temperatures. In the case of cyclopropane and cyclobutane the theory leads to the conclusion that 20 degrees of freedom form a heat reservoir which feeds the energy into the carbon bond that is to break and that this rate becomes controlling above about 1200°K. This would correspond to 20 of the 21 vibrational bonds of cyclopropane feeding energy into the carbon bond that is to break, and there would be no noticeable rise in the number of bonds for cyclobutane. This theory is especially important for shock tubes and detonations, where this falling-off from the extrapolated low temperature rate becomes glaringly obvious.

"Slow vibrationally activated reactions at high temperatures", by Henry Eyring, Priestley Medal Address, April 7, 1975.

In this Priestley address I used starvation kinetics to explain slow reaction rates in explosives.

"A Limitation to the Mixed Potential Concept of Metal Corrosion", by T. N. Andersen, M. H. Ghandehari, and H. Eyring, J. Electrochem. Soc. 122, 1580-1585 (1975).

The corrosion of copper in oxygenated sulfuric acid solutions was studied by means of weight-loss and polarization curves. At a given potential, the rate of copper dissolution is greater in the presence than in the absence of oxygen reduction, which is contrary to the conventional theory of mixed potentials. An explanation of this phenomena is proposed on the basis of chemical attack by dissolved oxygen on the Cu^+ ions which are intermediates in the electrochemical copper oxidation scheme. The model is further verified by results of varying the solution agitation rate, acid strength, and oxygen partial pressure.

"The Electrochemical Reduction of Oxygen on Copper in Dilute Sulphuric Acid Solutions", by M. H. Ghandehari, T. N. Andersen, and H. Eyring, Corr. Sci. 16, 123-135 (1976).

The electrolytic reduction of O_2 on Cu was studied in dilute H_2SO_4 by steady-state and transient electrochemical techniques. A distinctive hump (i.e. a current maximum) is observed in the steady-state potentiostatic polarization curve approximately 50 mV negative to the open-circuit corrosion potential. Results of transient studies, of varying the solution agitation, and varying the concentrations of oxygen, sulphuric acid, and sulphate ions indicate that

the hump is due to cathodic film formation which inhibits the rate of oxygen reduction. The inhibiting film appears to be composed of intermediates from the O_2 reduction process and also may contain adsorbed sulphate ions. The film is removed under corrosion conditions by rapid dissolution of the substrate copper. Extrapolation of the cathodic Tafel curve to the corrosion potential yields corrosion rates lower than those measured because of the cathodic passivation.

"Significant structure theory applied to phase separation", by Suck-Hyun Lee, Mu Shik Jhon, and Henry Eyring, Proc. Natl. Acad. Sci. USA 74, 10-12 (1977).

The significant structure theory of liquids has been applied to the partially miscible system of the O_3 - O_2 mixture, which exhibits partial miscibility in the temperature range from -195.5°C to -179.9°C . The thermodynamic condition for phase separation is given by the following inequality:

$$\left(\frac{\partial^2 G_{\text{mixture}}}{\partial X_i^2} \right)_{T,P} < 0.$$

A partition function for the binary liquid mixture is developed using significant liquid structure theory. Here X_i is the mole fraction of either of the two components. We obtain the coexistence curve of the O_3 - O_2 system by varying the mole fractions of the components to find the temperature at which the two liquids separate. The agreement between theory and experiment is satisfactory.

"Effects of Oxygen on the Mechanism of Cadmium Dissolution in Sulfate Solutions", by T. N. Andersen, M. H. Ghandehari, E. Feng, and H. Eyring, J. Electrochem. Soc. 124, 977-981 (1977).

The dissolution rate of cadmium was measured in various nitrogen- and oxygen-saturated acidic sulfate solutions under potentiostatic conditions. At a given potential, the dissolution rate was found to be greater in O_2 - than in N_2 -saturated solutions. A dissolution mechanism is proposed which explains this phenomena as well as results from tests in which potential, solution agitation, and solution composition were varied. According to this mechanism Cd^+ ions are formed as intermediates and are then oxidized to the product Cd^{+2} ions by a chemical path involving O_2 as well as by the conventional electrochemical path.

"Prediction of Atmospheric Corrosion Rates"

Atmospheric corrosion of army equipment protected by a metal coating such as zinc or cadmium can be predicted with useful engineering accuracy by our equation $S = (1 + \exp k_1(\frac{t}{w} - \tau_1))^{-1}$. Here S is the fractional life time of the protective coating and t and w are the age and weight per unit area of the coating respectively. The two parameters k_1 and τ_1 are the rate of corrosion and half life respectively for a particular region when $w=1$ and must at present be determined by two experimental measurements for each type of climate. However, when these two measurements are made and the parameters determined the resulting equation has highly useful predictive value of corrosion resistance for this area.